4-nitro-*syn*-(*cis*-2,3-dimethylcyclopropyl)benzene (mp 43–45° after sublimation). The nmr spectra of the 2 isomer, 0.80 (6 H, d, J = 5 Hz), 1.0–1.5 (2 H, br m), 2.20 (1 H, t, J = 8 Hz), 7.25 (3 H, s), 7.55–7.82 (1 H, m), and the known 4 isomer, 0.8 (6 H, d, J = 5 Hz), 1.0–1.5 (2 H, br m), 2.20 (1 H, t, J = 8 Hz), 7.25 (3 H, s), 7.55–7.82 (1 H, m), distinguished the reaction products.

Nitro-*anti*-(*cis*-2,3-dimethylcyclopropyl)benzene. The nitration of *anti*-(*cis*-2,3-dimethylcyclopropyl)benzene at −15 to 0° produced, in near quantitative yield, an 80:20 mixture of the known[38] 2-nitro-*anti*-(*cis*-2,3-dimethylcyclopropyl)benzene, a yellow liquid, and 4-nitro-*anti*-(*cis*-2,3-dimethylcyclopropyl)benzene (mp 109–110° after sublimation). These compounds were also distinguished by the characteristic nmr spectra of the 2 isomer, 1.2 (8 H, s), 1.65 (1 H, d, J = 4.5 Hz), 6.95–7.45 (3 H, m), 7.61–7.83 (1 H, m), and the known 4 isomer, 1.23 (9 H, s), 7.05 (2 H, d, J = 8.5 Hz), 8.06 (2 H, d, J = 8.5 Hz).

Relative Rates. In a typical competitive experiment cyclopropylbenzene (0.118 g, 1.00 mmol) and toluene (0.920 g, 9.98 mmol) were weighed into a flask. Methylene chloride was added to bring the volume to 10 ml. In another flask, anhydrous nitric acid (0.061 g, 0.963 mmol, previously distilled from a twofold excess of sulfuric acid in a glass apparatus *in vacuo*) was added to acetic anhydride (0.151 g, 1.48 mmol) which had been purified by fractionation. This latter solution was maintained at ambient temperature for 15 min for the conversion of starting materials to acetyl nitrate. The solution was then diluted to 10-ml volume with methylene chloride. Both flasks were cooled to −25°. The contents of the flasks were then mixed in a third flask prechilled to −25°. The reaction was allowed to proceed 12 hr. An analytical reference compound, 3-nitro-1,2-dimethylbenzene (0.028 g, 0.210 mmol), was added to the reaction mixture. The solution was poured into water (500 ml). The organic layer was separated. The aqueous phase was extracted with three portions of ether (50 ml). The organic layers were combined and the solution was washed with distilled water (three 25-ml portions) prior to drying over magnesium sulfate. The solution was concentrated by removal of the solvents *in vacuo*. The product-rich residue was analyzed by vpc on a Carbowax 20M column (10 ft × 1/4 in.) operated at 200° with a helium flow of 100 ml/min.

Prior analytic work established that 2- and 4-nitrocyclopropylbenzene were not decomposed or otherwise fractionated in the isolation procedure. Thermal conductivity response factors were determined by the chromatography of three known mixtures containing 3-nitro-1,2-dimethylbenzene, the three isomeric nitrotoluenes, and the two major nitrocyclopropylbenzenes. The nitro compounds used in these calibration experiments were isomerically pure. At least two analyses of each mixture were carried out and the results averaged. The areas under the curves were measured by triangulation or by recorder integration. Both methods gave sensibly identical results.

Analysis of the product mixture described above revealed 62% conversion of nitric acid to nitroaromatic compounds. The Ingold–Shaw rate expression was used to assess the relative rate $k_{C_6H_5C_3H_5}/k_{C_6H_5CH_3}$ = 10.3 on the measured formation of 0.315 mmol of nitrotoluenes and 0.282 mmol of nitrocyclopropylbenzenes. A second experiment indicated the relative rate was 10.1.

The isomer distributions were determined in separate experiments conducted under the conditions of the kinetic experiments. The pure isomers were used to identify the reaction products and to determine the vpc response factors. In the course of this study Hahn and his students communicated the isomer distributions for spiro(cyclopropane-1,1′-indan) and 3′,4′-dihydrospiro(cyclopropane-1,1′(2*H*′)-naphthalene). Preliminary experiments indicated that three products were obtained in significant amounts in the nitration of the spiroindan. The 5-nitro derivative constituted 83% of these products. This result was combined with the results of Hahn and his associates to yield the values reported in Table II. The isomer distribution for the nitration of the spirotetralin was established in the same way.

Acknowledgment. We are particularly indebted to G. L. Closs for his assistance and many valuable discussions of the chemistry of cyclopropanes and to R. C. Hahn for his careful examination of this article.

Mechanisms of Ion–Molecule Reactions of Propene and Cyclopropane[1]

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Abstract: Ion–molecule reaction of the $C_3H_6\cdot^+$ ion from propene proceeds *via* a "four-center" mechanism to a $C_6H_{12}\cdot^+$ ion capable of 1,2- and 1,4-hydrogen migrations but not 1,3-hydrogen migration. The $C_6H_{12}\cdot^+$ ion can rearrange *via* structures **6**, **7**, and **8**. Decomposition to ethylene proceeds *via* a "four-center" cleavage of the dimethylcyclobutane ion **6**. The $C_3H_6\cdot^+$ ion from cyclopropane can be distinguished from that formed from propene. The $C_6H_{12}\cdot^+$ ion formed on reaction of propene and cyclopropane is different from that formed from propene alone; it undergoes facile cleavage with loss of ethylene. By study of ion–molecule reactions of $CD_3CHCH_2\cdot^+$ formed at energies below the appearance potential of fragment ions a small amount of isotopic scrambling has been observed in the $CD_3CHCH_2\cdot^+$ ion in accord with predictions based on quasiequilibrium theory. Part of the $C_3H_3^+$ ions formed from propene are unusually unreactive at high pressures with propene and may have the cyclopropenium ion structure.

The ion–molecule reactions in unsaturated systems, particularly hydrocarbon systems, offer an excellent opportunity to study in detail the mechanisms and kinetics of an important class of condensation phenomena. Most studies have been carried out using standard high-pressure mass spectroscopy although more recently time of flight, tandem techniques, and ion cyclotron resonance (icr) techniques have become more widely used. In our studies, the icr technique has been employed.[2]

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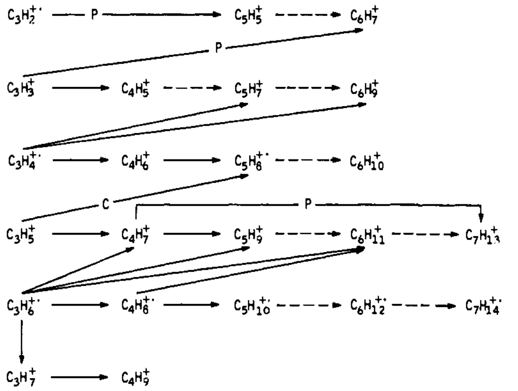

Figure 1. Principle reactions in propene and cyclopropane. Solid arrows indicate that a double resonance signal was observed for the reaction. Double resonance signals were not observable for reactions indicated by dashed arrows. P indicates that a double resonance signal was observed only in the propene system; C, only in the cyclopropane system.

Studies of ion–molecule reactions of ethylene[3a] and allene and propyne[3b] have led to the hypothesis of "four-center" mechanisms in the decomposition of the intermediate complexes. Isotopic labeling experiments have confirmed this hypothesis in the allene and propyne reactions but the symmetry of ethylene makes mechanistic conclusions based on labeling experiments inconclusive. To elucidate the mechanism of the condensation and isotopic scrambling reactions of olefins, we have investigated the reactions of the less symmetrical propene radical cation with propene and cyclopropane. Our conclusions are compared to related studies of other workers on propene[4–9] and cyclopropane.[6,9–11]

Experimental Section

The general experimental icr techniques have been discussed in detail by several authors[2,3] and will not be recounted here. The experiments reported here were performed on similar icr machines at both the Jet Propulsion Laboratory[3,12] and at the University of California at Santa Barbara.[13] Pressure was measured on an MKS Baratron Series 90 capacitance manometer. The proton transfer rate $CH_4\cdot^+ + CH_4 \rightarrow CH_5^+ + \cdot CH_3$ was measured to be 1.24 (UCSB) and 1.16 (JPL) $\times 10^{-9}$ cm^3 molecule^{-1} sec^{-1} in good agreement with literature values.[14] The propene gas was Philips Petroleum Research Grade, cyclopropane was Matheson Co., and the deuterated species were Merck Sharpe and Dohme.

Results and Discussion

General Reaction Scheme in Propene and Cyclopropane. The general reaction scheme is given in Figure 1. These results were determined by variation of electron energy, pressure plots, and double resonance. There are two characteristic condensation reactions of the primary ions

$$R\cdot^+ + C_3H_6 \longrightarrow [RC_3H_6\cdot^+]^* \longrightarrow RCH_2\cdot^+ + C_2H_4 \qquad (1)$$

and

$$R\cdot^+ + C_3H_6 \longrightarrow [RC_3H_6\cdot^+]^* \longrightarrow RC_2H_3^+ + \cdot CH_3 \qquad (2)$$

The first reaction is observed for every primary C_3 fragment ion ($C_3H_6\cdot^+$, $C_3H_5^+$, $C_3H_4\cdot^+$, $C_3H_3^+$, $C_3H_2\cdot^+$, $C_3H_1^+$) and yields the most abundant product ions. The second reaction is observed in significant amounts only for the radical ions $C_3H_6\cdot^+$, $C_3H_4\cdot^+$, and $C_3H_2\cdot^+$. The radical ions appear to be considerably less efficient in eliminating C_2H_4 *via* reaction 1 than the even-electron ions. This result possibly reflects the effect of the competitive reaction 2 available to the radical ions.

The $C_3H_3^+$ ion is interesting in that it only partially reacts (*ca.* 50%) with neutral propene or cyclopropane to form $C_4H_5^+$. The implication is that two forms of $C_3H_3^+$ with different energies exist, possibly one cyclic form and one linear form. Nonoccurrence of reaction 3 suggests that $\Delta H_f(C_3H_3^+) \leq 245$ kcal/mol. Recent

$$C_3H_3^+ + C_3H_6 \longrightarrow C_4H_5^+ + C_2H_4 \qquad (3)$$

monoenergetic electron impact studies on cyclopropene and propargyl radical ($HC{\equiv}CCH_2\cdot$)[15] indicate $\Delta H_f(C_3H_3^+) = 256 \pm 2$ kcal/mol corroborating photoionization AP values of $C_3H_3^+$ from larger molecules.[16] The interpretation is that $C_3H_3^+$ with an AP of 256 kcal/mol is cyclic.[15] The nonoccurrence of reaction 3 indicates either the $C_3H_3^+$ ions formed from electron or photon impact are vibrationally excited or there is a significant barrier to reaction 3.

Reaction of the Parent Ions. The thermal energy product distributions are given in reaction 4 and agree

$C_3H_6\cdot^+ + C_3H_6 \longrightarrow$

			% from C_3H_6	% from c-C_3H_6	% from C_3D_6
$\rightarrow C_3H_7^+$	+	$\cdot C_3H_5$	24	11	13
$\rightarrow C_4H_7^+$	+	$\cdot C_2H_5$	13	13	9
$\rightarrow C_4H_8\cdot^+$	+	C_2H_4	43	73	48
$\rightarrow C_5H_9^+$	+	$\cdot CH_3$	20	3	30

(4)

with previous low-energy data for propene[4a,9,17a] and cyclopropane.[6,9] The total rate for reaction 4 was measured to be $7.4 \pm 1.0 \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1} for propene and $3.3 \pm 1.0 \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1} for cyclopropane. The propene rate agrees with measurements of other workers,[4a,6,18] while the cyclopropene value is somewhat higher than that previously reported.[6] Our measurements were made using the

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(2) For recent reviews, see J. D. Baldeschwieler, *Science*, **159**, 263 (1968); G. Gray, *Advan. Chem. Phys.*, **19**, 141 (1971).

(3) (a) M. T. Bowers, D. D. Elleman, and J. L. Beauchamp, *J. Phys. Chem.*, 72, 3599 (1968); (b) M. T. Bowers, D. D. Elleman, R. M. O'Malley, and K. R. Jennings, *ibid.*, **74**, 2583 (1970).

(4) (a) F. P. Abramson and J. H. Futrell, *ibid.*, **72**, 1994 (1968); (b) *ibid.*, **72**, 1826 (1968).

(5) A. G. Harrison, *Can. J. Chem.*, **41**, 236 (1962).

(6) A. A. Herod and A. G. Harrison, *J. Phys. Chem.*, **73**, 3189 (1969), and references therein.

(7) A. M. Peers, *ibid.*, **73**, 4141 (1969).

(8) I. Kayaro, I. Omura, and I. Tanaka, *J. Chem. Phys.*, **44**, 3850 (1966).

(9) A. A. Herod, A. G. Harrison, R. M. O'Malley, A. J. Ferrer-Correia, and K. R. Jennings, *J. Phys. Chem.*, **74**, 2720 (1970).

(10) A. G. Harrison and J. M. S. Tait, *Can. J. Chem.*, 40, 1986 (1962).

(11) R. F. Pottie, A. J. Forquet, and W. H. Hamill, *J. Amer. Chem. Soc.*, **84**, 529 (1962).

(12) M. T. Bowers, D. D. Elleman, and J. King, Jr., *J. Chem. Phys.*, 50, 1840, 4787 (1969).

(13) M. T. Bowers and P. R. Kemper, *J. Amer. Chem. Soc.*, **93**, 5352 (1971).

(14) S. K. Gupta, E. G. Jones, A. G. Harrison, and J. J. Myher, *Can. J. Chem.*, **45**, 3107 (1967).

(15) F. P. Lossing, private communication.

(16) A. C. Parr and F. A. Elder, *J. Chem. Phys.*, **49**, 2659 (1968).

(17) (a) J. M. S. Henis, *ibid.*, **52**, 282 (1970); (b) *ibid.*, **52**, 292 (1970).

(18) L. W. Sieck and S. K. Searles, *J. Amer. Chem. Soc.*, **92**, 2937 (1970). The rate reported here is for C_3D_6.

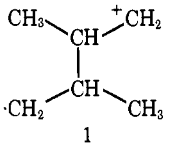
Table I. Isotopic Product Distributions from Various $[C_6H_6D_6{}^+]^*$ Complexes in Propene and Cyclopropane Mixtures[a]

Products	$CD_3CD{=}CD_2 + CH_3CH{=}CH_2$		$CD_3CH{=}CH_2$	$CD_3CD{=}CD_2$ + c-C_3H_6	Random
	Icr this work	Tandem mass spectrometer[c]			
$C_5H_6D_3{}^+ + \cdot CD_3$	0.24	0.25	0.37	0.31	0.05
$C_5H_5D_4{}^+ + \cdot CHD_2$	0.28	0.25	0.22	0.16	0.45
$C_5H_4D_5{}^+ + \cdot CH_2D$	0.26	0.22	0.16	0.29	0.45
$C_5H_3D_6{}^+ + \cdot CH_3$	0.23	0.28	0.25	0.23	0.05
$C_4H_6D_2\cdot{}^+ + C_2D_4$	0.09[b]	0.06[c]	0.09[b]	0.01[b]	0.03
$C_4H_5D_3\cdot{}^+ + C_2HD_3$	0.25[b]	0.23[c]	0.06[b]	0.04[b]	0.24
$C_4H_4D_4\cdot{}^+ + C_2H_2D_2$	0.28[b]	0.29[c]	0.46[c]	0.12[b]	0.45
$C_4H_3D_5\cdot{}^+ + C_2H_3D$	0.31[b]	0.28[c]	0.16[b]	0.16[b]	0.24
$C_4H_2D_6\cdot{}^+ + C_2H_4$	0.09[b]	0.14[c]	0.23[c]	0.68[b]	0.03

[a] All data were taken at electron energies below the appearance potential of any fragment ion. Approximately 1:1 mixtures were used. [b] A certain amount of interference arises from $C_4(H,D)_7{}^+$ ions. Approximate corrections have been made assuming a symmetrical isotopic distribution pattern in the $C_4(H,D)_7{}^+$ products and a 4:1 ratio of $C_4(H,D)_8{}^+$ to $C_4(H,D)_7{}^+$ products. [c] The tandem mass spectral data[4a] were corrected as in footnote *b* but the $C_4(H,D)_8{}^+$ to $C_4(H,D)_7{}^+$ ratio used was 2:1.

technique of Buttrill[19] programmed for an iterative solution on a digital computer.

We will now consider in detail the reaction of the parent ion in propene. At low energies, the skeletal condensation reactions[20] of the parent $C_3H_6\cdot{}^+$ ions most likely proceed through a $[C_6H_{12}\cdot{}^+]^*$ complex intermediate with a lifetime of a few rotations or more.[21] The principle condensation products correspond to loss of C_2H_4 and $\cdot CH_3$ from the $[C_6H_{12}\cdot{}^+]^*$ complex *via* reactions 1 and 2 above. Structures **1** and **2** for the $[C_6H_{12}\cdot{}^+]^*$ intermediate have been proposed by Abramson and Futrell.[4a,4b] The linear structure **2** was suggested by comparison with energy-dependent fragmentation patterns of a large number of C_6H_{12} compounds[4b] and is Abramson and Futrell's preferred choice. The spectra of 3-hexene most closely resembled their product distribution and were the basis of their



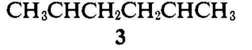
1

$CH_3CH_2\overset{+}{C}HCHCH_2CH_3$

2

choice of the linear form. We find our thermal energy product distribution fits equally well with the published[4b] clastogram for either 2- or 3-hexene close to threshold and also closely fits the 1,2-dimethylcyclobutane clastogram near threshold.[22] Rearrangements of these ions make a structural assignment based solely on clastograms doubtful, however.

Peers[7] has suggested a linear structure for the $[C_6H_{12}\cdot{}^+]^*$ intermediate that differs slightly from that of Abramson and Futrell

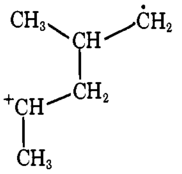


$CH_3\dot{C}HCH_2CH_2\overset{+}{C}HCH_3$

3

Peers argues that structure **3** is superior to **2** because no net H-atom shift is necessary if C_2H_4 is to be eliminated. It should be pointed out that structure **2** is superior to structure **3** for loss of ethyl radicals for the same reason. Loss of $\cdot C_2H_5$, however, comprises only 12% of the product distribution in the $C_3H_6\cdot{}^+$-propene system compared with 48% for loss of C_2H_4. Peers further prefers **3** over **1** as loss of C_2H_4 from **1** requires breaking two carbon–carbon bonds while loss of C_2H_4 from **1** requires breaking only one carbon–carbon bond.

Henis[17] has studied the condensation reactions in monoolefins and has concluded that (1) no significant rearrangement of the parent ions occurs in the complex formation; (2) addition occurs at either end of the double bond; (3) fragmentation involving more than one bond is not favorable. On the basis of Henis' rules structure **3** appears appealing. However, since addition can occur at either end of the double bond, structure **4** is also possible.



4

Mechanism of Deuterium Scrambling in Propene Condensation. It is clear that considerable doubt remains regarding the structure(s) of the $[C_6H_{12}\cdot{}^+]^*$ complex(es) in the propene condensation reactions. For this reason, we observed the isotopic product distributions for the ethylene and methyl radical eliminations with $CH_3CH{=}CH_2$, $CD_3CD{=}CD_2$, and $CD_3CH{=}CH_2$. The results are tabulated in Tables I, II, and III. Detailed consideration of these isotopic product distributions led us to postulate Scheme I to describe the reactions of $C_6H_6D_6\cdot{}^+$ from the $CH_3CH{=}CH_2 + CD_3CD{=}CD_2$ mixture.

In Scheme I the initially formed $C_3H_6D_6\cdot{}^+$ complex is assumed to be **5**, since this should be the most stable of the three possible initial stepwise addition products **5**, **7**, and **9**. By 1,2-alkyl and 1,2-hydrogen migrations[23,24] structures **9** and **8** should be accessible. If

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(19) S. E. Buttrill, Jr., *J. Chem. Phys.*, **50**, 4125 (1969); A. G. Marshall and S. E. Buttrill, Jr., *ibid.*, **52**, 2752 (1970).

(20) Skeletal condensation reactions require the breaking and/or forming of one or more carbon–carbon bonds. These reactions are distinct from proton transfer or hydride ion abstraction reactions which often proceed *via* a direct mechanism or a "loose" complex [J. J. Myher and A. G. Harrison, *J. Phys. Chem.*, **72**, 1905 (1968)].

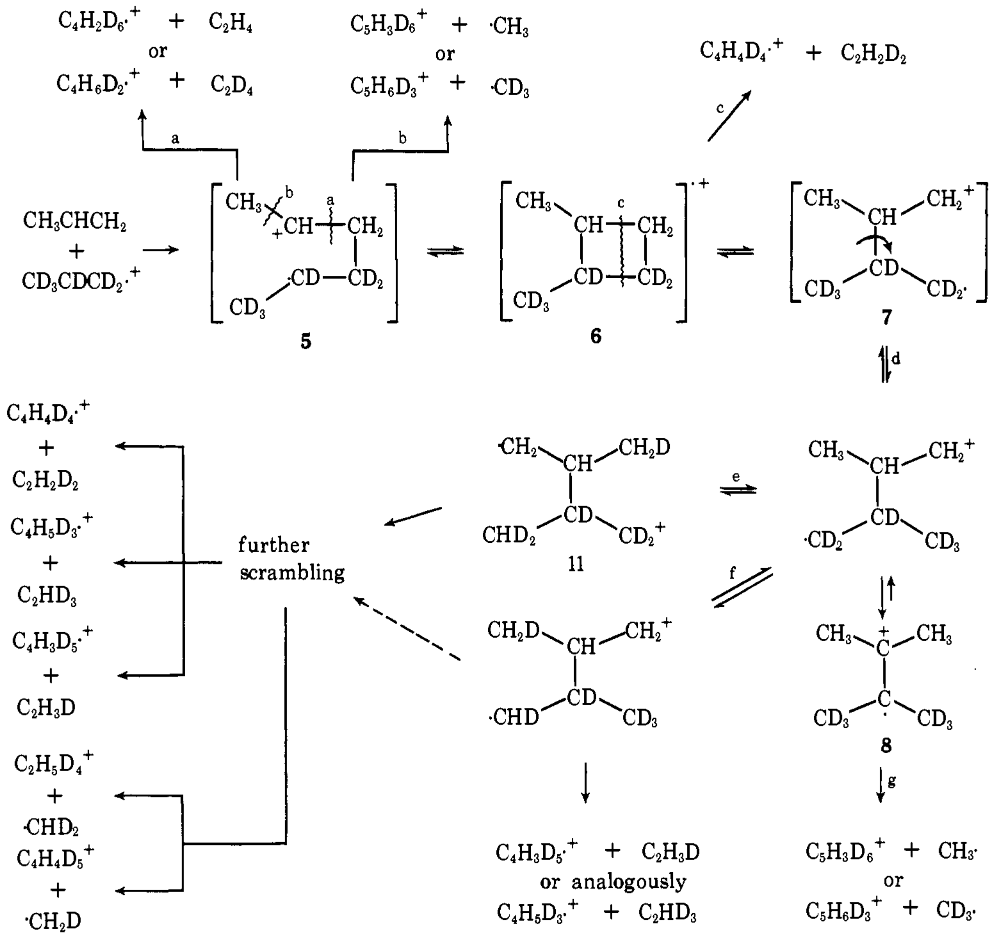
(21) Z. Herman, A. Lee, and R. Wolfgang, *J. Chem. Phys.*, **51**, 452 (1969).

(22) D. H. Aue and M. T. Bowers, unpublished data.

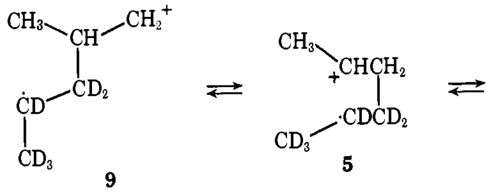
(23) While 1,2-hydrogen and alkyl migrations are rare in radical rearrangements [W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, pp 280–285)], they are well known in carbonium ion rearrangements and might be expected to occur in radical cations.

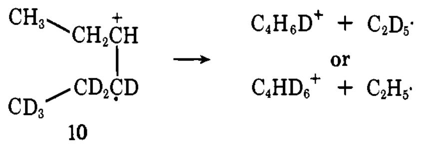
(24) Such 1,2 migrations may be responsible for isotopic scrambling in deuterated propenes and butenes: (a) S. R. Smith, R. Schor, and W. P. Norris, *J. Phys. Chem.*, **69**, 1615 (1965); (b) W. H. McFadden, *ibid.*, **67**, 1074 (1963); (c) H. H. Voge, C. D. Wagner, and D. D. Stevenson,

Scheme I



structure **10** were reached it should decompose primar-

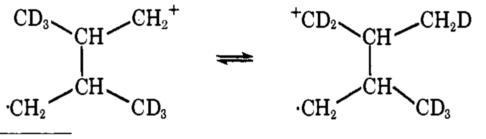




ily with loss of an ethyl radical[25] while structure **8** would be expected to strongly favor loss of methyl radical.[26]

Fragmentation of **5** would be expected to give ethylene *via* path a and methyl radical *via* path b. Structure **6** can undergo a reverse 2 + 2 cycloaddition, path c, providing an alternative to path a for ethylene formation.[27]

The fragmentation products from the $C_6H_6D_6\cdot^+$ complex from $CH_3CHCH_2\cdot^+$ and CD_3CDCD_2, Table I, clearly reflect more than a random H,D exchange but cannot be explained by any single intermediate or fragmentation mechanism. Consider the distribution of products from loss of a methyl radical. The near equality of all the isotopic fragments departs from the distribution expected from fragmentation by path b or from structure **8**, either of which should lose only $CH_3\cdot$ and $CD_3\cdot$. The other fragments, from loss of $CH_2D\cdot$ and $CHD_2\cdot$, can be nicely explained by assuming that isotopic scrambling can occur by one or more 1,4-hydrogen shifts,[24,28] pathways e and f. A scheme analogous to Scheme I for CD_3CHCH_2 can also explain the product distribution for loss of methyl radical in this propene. The CD_3CHCH_2 data suggest that the direct loss of $CD_3\cdot$ *via* path b is probably a minor process accounting for at most 10–15% of the methyl loss. The large amount of $CH_3\cdot$ loss indicates that structure **8**, which should give equal amounts of $CD_3\cdot$ and $CH_3\cdot$ loss, is responsible for as much as 40–50% of reaction before isotopic scrambling occurs. The $CH_2D\cdot$ and $CHD_2\cdot$ loss can again be accounted for by 1,4-hydrogen shifts, pathways e and f. *Although the scrambling for CD_3CHCH_2 could also be explained by 1,3-hydrogen shifts such as reaction 5 this pathway*


(5)

J. Catal., 2, 58 (1963); (d) G. G. Meisels, J. Y. Park, and B. G. Giessner, *J. Amer. Chem. Soc.*, **91**, 1555 (1969); (e) W. A. Bryce and P. Kebarle, *Can. J. Chem.*, **34**, 1249 (1956); (f) B. J. Millard and D. F. Shaw, *J. Chem. Soc. B*, 664 (1966).

(25) The mass spectrum of 3-hexene shows primary loss of ethyl radical at high electron energy; see ref 4b.

(26) The mass spectrum of tetramethylethylene shows almost exclusive loss of methyl radical up to 100-eV electron beam energy. This suggests that formation of **8** in Scheme I is not readily reversible.

(27) The mass spectrum of 1,2-dimethylcyclobutane, *cf.* structure **6**, shows primary loss of ethylene and an energy dependence for methyl radical and ethyl radical loss similar to the clastogram of cyclohexane.[4b]

(28) Such 1,4-hydrogen shifts are common in radical reactions (see ref 23).

Table II. Isotopic Product Distributions from $[C_6H_6D_6\cdot^+]^*$ Complexes from Specific Propene and Cyclopropane Ions[a]

Products	$CH_3CHCH_2\cdot^+$ + CD_3CDCD_2	$CD_3CDCD_2\cdot^+$ + CH_3CHCH_2	$CD_3CDCD_2\cdot^+$ + c-C_3H_6	c-$C_3H_6\cdot^+$ + CD_3CDCD_2	Random
$C_5H_6D_3^+$ + $\cdot CD_3$	0.26	0.27	0.35	0.39	0.05
$C_5H_5D_4^+$ + $\cdot CHD_2$	0.25	0.25	0.14	0.13	0.45
$C_5H_4D_5^+$ + $\cdot CH_2D$	0.26	0.24	0.33	0.24	0.45
$C_5H_3D_6^+$ + $\cdot CH_3$	0.23	0.24	0.18	0.24	0.05

[a] Resonant ion ejection was employed in obtaining all of these product distributions. Data were taken below the appearance potential of any fragment ions.

Table III. Isotopic Product Distributions from $[C_6H_9D_3\cdot^+]^*$ Complexes from CD_3CHCH_2 plus CH_3CHCH_2 and c-C_3H_6[a]

Products	$CD_3CHCH_2\cdot^+$ + CH_3CHCH_2	$CH_3CHCH_2\cdot^+$ + CD_3CHCH_2	$CD_3CHCH_2\cdot^+$ + c-C_3H_6	c-$C_3H_6\cdot^+$ + CD_3CHCH_2	Random
$C_5H_9^+$ + $\cdot CD_3$	0.19	0.43	0.32	0.61	0.01
$C_5H_8D^+$ + $\cdot CHD_2$	0.10	0.05	0.07	0.07	0.25
$C_5H_7D_2^+$ + $\cdot CH_2D$	0.19	0.07	0.08	0.10	0.62
$C_5H_6D_3\cdot^+$ + $\cdot CH_3$	0.52[b]	0.45[b]	0.53[b]	0.23[b]	0.12

[a] Resonant ion ejection was employed in obtaining all of these product distributions. [b] Low product intensities in the cyclopropane experiments make that data only qualitative. Data were taken below the appearance potential of any fragment ions.

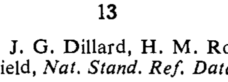
cannot lead to scrambling in the $C_3H_6\cdot^+$ + C_3D_6 system. If 1,3 shifts were significant then there should be more isotopic scrambling in the CD_3CHCH_2 system than in the $C_3H_6\cdot^+$ + C_3D_6 system. In fact, the methyl loss data indicate that there is slightly less scrambling for CD_3CHCH_2. Therefore, 1,3 shifts are not very important scrambling pathways.[29] There is evidence however, in Table III to be discussed later that a small amount (15–20%) of 1,3-hydrogen migration occurs in the $CD_3CHCH_2\cdot^+$ ion *before* condensation.

The elimination of ethylene in the $C_3H_6\cdot^+$ + C_3D_6 system might be explained by assuming that the large amounts of C_2H_4 and C_2D_4 elimination relative to random are the result of direct elimination of ethylene *via* path a from the initial intermediate **5**. It can be seen that such a process in the CD_3CHCH_2 system would lead specifically to C_2H_3D and C_2HD_3 loss. In the product distribution for CD_3CHCH_2, however, these products are minor (16 and 6%). Therefore, path a appears not to be a significant contributor to ethylene loss.

A mechanism for ethylene elimination which explains both the $C_3H_6\cdot^+$ + C_3D_6 and CD_3CHCH_2 data is provided by assuming that fragmentation of **6** *via* path c is the primary source of ethylene elimination. A maximum of 28% of the ethylene loss can be explained by direct elimination of $C_2H_2D_2$ from **6** in the $C_3D_6\cdot^+$ + C_3H_6 system. Reversible reactions d, e, and f can lead to isotopic scrambling followed by recyclization to scrambled versions of **6** and elimination of the other isotopically substituted ethylenes, C_2H_4, C_2H_3D, C_2HD_3, and C_2D_4. This scheme is also consistent with the CD_3CHCH_2 data, where the product, C_2H_4, of direct fragmentation *via* path c can account for 23% of the products. The 46% $C_2H_2D_2$ product and the C_2H_3D, C_2HD_3, and C_2D_4 must then come from isotopic scrambling. The scrambling in these products has clearly not reached the random distribution. Deuterium scrambling appears to be incomplete and specific in both the $C_3D_6\cdot^+$ + C_3H_6 and the CD_3CHCH_2 systems.

The isotopic scrambling scheme presented above is capable of semiquantitatively explaining the data presented. It represents the least complicated mechanism necessary to explain the data and requires that intermediates **6**, **7**, and **8** be involved, that the 1,2-hydrogen shifts give **8**, and that the 1,4-hydrogen shifts (paths e and f) in **7** occur. While other types of hydrogen migrations and carbon rearrangements might occur to a small extent they are not required to explain the data. In particular, 1,3 rearangements are less favorable than 1,4 and 1,2 shifts.

Some energy relationships in Scheme I are expressed in the partial potential energy surface in Figure 2. This diagram is consistent with our data and known thermodynamic data.[30] In addition, the nature of the dimethylcyclobutane ion, **6**, in Scheme I was investigated by measuring its appearance potential.[22] It was found that its appearance potential (*ca.* 10.5 eV) was the same as that for the product ions $C_3H_6\cdot^+$, $C_4H_8\cdot^+$, and $C_5H_9^+$, which all form with essentially no barrier from $C_6H_{12}\cdot^+$. This puts the heat of formation of this ion at *ca.* 233 kcal/mol,[31] almost identical with the 234-kcal/mol value for $C_3H_6\cdot^+$ plus propene. Excess vibrational energy in $C_3H_6\cdot^+$ might contribute as much as 10–20 kcal of excess energy in the intermediate dimethylcyclobutane ion, **6**. This should provide enough internal energy to induce hydrogen scrambling and exothermic decomposition of this ion with loss of methyl radical, ethyl radical, and ethylene. The barrier to 1,4- and 1,2-hydrogen shifts must be comparable to the barriers for decomposition on the basis of the scrambling data. Evidence that 1,4- and 1,2-hydrogen shifts can occur in the 1,2-dimethyl-1,2-dideuteriocyclobutane ion **13**



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[29] In radical reactions, 1,4- and 1,5-hydrogen migrations are more favorable than 1,3 migrations (see, for example, ref 23).

[30] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Heron, K. Draxl, and F. H. Field, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. **26** (1969).

[31] The heat of formation of 1,2-dimethylcyclobutane was estimated from data of P. V. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Amer. Chem. Soc.*, **92**, 2377 (1970).

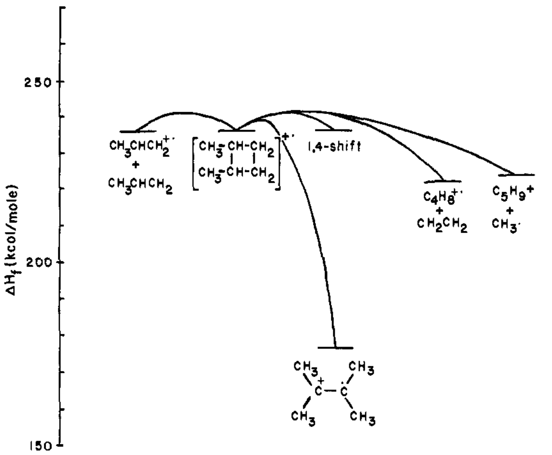


Figure 2. Potential energy surface for $CH_3CHCH_2\cdot^+$ + CH_3CHCH_2. Thermodynamic data from ref 22 and 30.

has been found in the mass spectral fragmentation of this labeled molecule.[22] It loses $\cdot CH_3$, $\cdot CH_2D$, and $\cdot CHD_2$ in a 2:2:1 ratio, C_2H_4, C_2H_3D, and $C_2H_2D_2$ in a 2:3:2 ratio, and C_3H_6, C_3H_5D, and $C_3H_5D_2$ in a 1:2:1 ratio at 12.0 eV. These data confirm the ion–molecule reaction data and suggest that the postulated mechanism is reasonable.

Use has been made of the "most stable isomer" criterion for determining complex intermediate structures in ion–molecule reactions[32] of simple unsaturated hydrocarbons in order to compare experimental product distributions with quasiequilibrium theory[33] (QET) calculations. The data and interpretation presented here indicate such an approach is certainly not valid for $C_3H_6\cdot^+$ + C_3H_6 where more than one important intermediate occurs on the potential surface for fragmentation.

In $CD_3CH{=}CH_2$ reactions 6 are observed

$$C_3D_3H_3\cdot^+ + CD_3CH{=}CH_2 \begin{cases} & & k_{rel} & \\ \nearrow & C_3D_4H_3^+ + C_3D_2H_3\cdot & 0.85 & (6a) \\ \searrow & C_3D_3H_4^+ + C_3D_3H_2\cdot & 0.15 & (6b) \end{cases}$$

Proton (or atom) transfer reactions of this type usually do not proceed *via* a long-lived complex but rather proceed *via* a direct type mechanism.[20] A direct mechanism is also supported by the observation of a positive double resonance signal for this exothermic reaction. The preference for D^+ transfer over H^+ transfer by a factor of six probably reflects the difference in the relative bond strengths of the allylic and vinylic C–H bonds.[34,35] The kinetic isotope effect for the proton transfer reaction above would favor H^+ transfer over D^+ transfer by a factor of about 2.[24a,36] The operation of this isotope effect can be seen by comparing the relative product distributions from C_3H_6 and C_3D_6 (reaction 4). The relative proportions of proton transfer product ($C_3H_7^+$) and the product ($C_4H_7^+$) from loss of ethyl radical are both depressed in the fully deuterated system. Thus, the transition states for proton transfer and ethyl loss must involve more C–H breaking than for methyl loss and elimination of ethylene. This is to be expected from the proposed direct mechanism for reaction 6, from the mechanism for ethyl loss from **10**, and from the mechanisms for methyl and ethylene loss discussed in connection with Scheme I.

Structure of the $C_3H_6\cdot^+$ Ion from Cyclopropane. The principal condensation reactions in cyclopropane are qualitatively very similar to those in propene. The basic differences are the general unreactivity of the cyclopropane relative to propene ($k_{c\text{-}C_3H_6}/k_{\text{propene}} \cong 0.45$) and the predominant loss of ethylene at the expense of methyl loss (at least in reactions of the parent *c*-$C_3H_6\cdot^+$ ions). An interesting comparison is the relative rate of methyl radical elimination *via* reactions 7–9.

$$C_3H_6\cdot^+ + C_3H_6 \longrightarrow C_5H_9^+ + \cdot CH_3 \qquad (7)$$

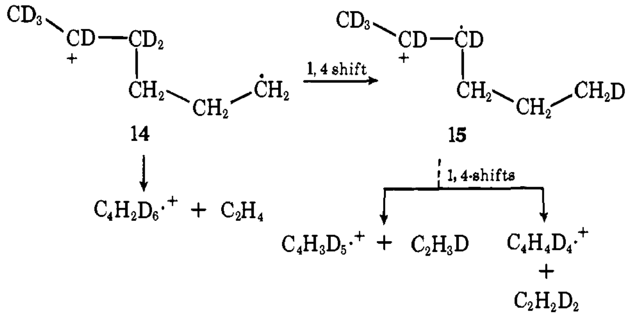
$$C_3H_4\cdot^+ + C_3H_6 \longrightarrow C_5H_7^+ + \cdot CH_3 \qquad (8)$$

$$C_3H_2\cdot^+ + C_3H_6 \longrightarrow C_5H_5^+ + \cdot CH_3 \qquad (9)$$

The approximate relative rates $k_{C_3H_6\cdot^+}:k_{C_3H_4\cdot^+}:k_{C_3H_2\cdot^+}$ in propene are 0.53:1.00:0.82 and in cyclopropane are 0.007:1.00:0.70. Field,[37] from appearance potential studies, suggested that the fragment ions in cyclopropane are open-chain species. His conclusions are not as firm with regard to the parent ion, although he does state that if the parent ion in cyclopropane is open chain it is $CH_2CH_2CH_2\cdot^+$ rather than $CH_3CHCH_2\cdot^+$. Our data agree with this conclusion as $\cdot CH_3$ is apparently not conveniently available as a leaving group in the reaction of the parent $C_3H_6\cdot^+$ ion from cyclopropane.

Additional evidence that the $C_3H_6\cdot^+$ ion from cyclopropane has not rearranged to the $CH_3CHCH_2\cdot^+$ structure is found in the ion ejection experiments in Table II. It can be seen that the product distributions from $CD_3CDCD_2\cdot^+$ plus *c*-C_3H_6 and *c*-$C_3H_6\cdot^+$ plus CD_3CDCD_2 are nearly identical and quite different from those from $CH_3CHCH_2\cdot^+$. The data in Table III roughly support this conclusion but are complicated by the possibility of rearrangement in $CD_3CHCH_2\cdot^+$.[38]

Mechanism of Deuterium Scrambling in Reactions with Cyclopropane. The most striking feature of the product distribution of CD_3CDCD_2 and cyclo-



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(32) S. E. Buttrill, Jr., *J. Chem. Phys.*, **52**, 6174 (1970).

(33) (a) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Nat. Acad. Sci. U. S.*, **38**, 667 (1952); (b) for a recent review, see H. M. Rosenstock, *Advan. Mass. Spectrom.*, **4**, 523 (1968).

(34) V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medev, and V. L. Frankevich, "Bond Energies, Ionization Potentials and Electron Affinities," St. Martin's Press, New York, N. Y., 1966, p 56.

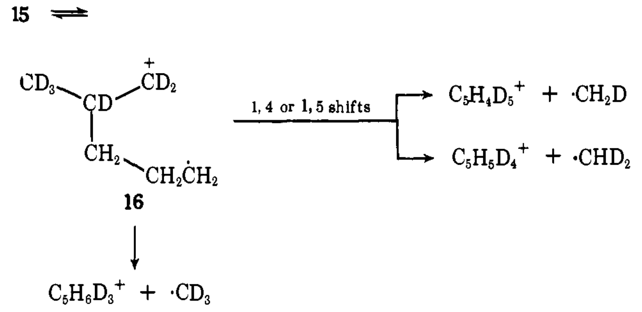
(35) The 15% H^+ transfer may be from 1,3 rearrangement in $CD_3CHCH_2\cdot^+$, *vide infra*.

(36) See, for example: F. S. Klein and L. J. Friedman, *J. Chem. Phys.*, **41**, 1789 (1964); H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1964; B. J.-S. Wang and E. R. Thornton, *J. Amer. Chem. Soc.*, **90**, 1216 (1968); I. Howe and F. W. McLafferty, *ibid.*, **93**, 99 (1971); F. W. McLafferty, private communication.

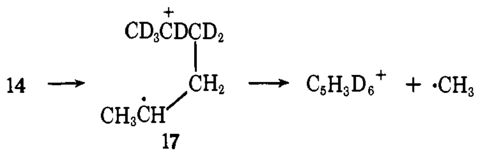
(37) F. A. Field, *J. Chem. Phys.*, **20**, 1734 (1952).

(38) A similar difference in $C_3H_6\cdot^+$ structures has been seen in ion–molecule reactions with ammonia by M. L. Gross and F. W. McLafferty, *J. Amer. Chem. Soc.*, **93**, 1267 (1971).

propane, Table I, is the specific (68%) loss of C_2H_4. This is the result of direct fragmentation of the initially formed ion **14**. The other major elimination products, C_2H_3D and $C_2H_2D_2$, come from scrambling *via* reversible 1,4-hydrogen shifts involving structure **15**.



The CD_3 loss comes directly from **14, 15** or **16**. The $CH_3\cdot$ loss appears to result from a 1,2-hydrogen shift of **14** to give **17** where the stability of the secondary radical favors the 1,2 migration. The loss of CH_2D and CHD_2 may result from 1,5 shifts or 1,4 shifts from **16**.



Deuterium Scrambling in $CD_3CHCH_2\cdot^+$. The ion ejection experiments summarized in Table II show that the product distribution is not substantially changed as a result of a change in the partner bearing the positive charge before reaction. This suggests that there is sufficient time in the intermediate complex to redistribute the internal energy before decomposition.[39] The data for $CD_3CHCH_2\cdot^+$ plus CH_3CHCH_2 in Table III, however, show a remarkable change in product distribution depending on the molecule bearing the initial charge. Since this cannot result from incomplete randomization of internal energy as discussed above, it must reflect partial isotopic rearrangement in the $CD_3CHCH_2\cdot^+$ ion. The direction of the change is nicely consistent with this conclusion. An additional 17% of the scrambled products (loss of $CHD_2\cdot$ and $CH_2D\cdot$) is formed with a concomitant decrease in the product of $CD_3\cdot$ loss. The data for cyclopropane are less clear because of the difference in the total internal energy depending on which partner is ionized and because the very low product intensities make the data only qualitative. A similar decrease in the $CD_3\cdot$ loss from reaction of $CD_3CHCH_2\cdot^+$ is consistent with scrambling in this ion.

Scrambling in $CD_3CHCH_2\cdot^+$ has been investigated previously by observing its consequences in fragment ion composition.[24a–d] It was noted that the extent of deuterium scrambling increased at low energies in the 15–50-eV range studied. Our results provide, for the first time, a method for observing such scrambling at energies below the appearance potential of fragment ions. The observation of some scrambling at these energies implies the barrier for scrambling in propene is lower than that for fragmentation. This confirms mechanistic interpretations based on quasiequilibrium theory to explain the energy dependence of unimolecular ionic decomposition products.[40]

Conclusions

Deuterium scrambling has often been observed in hydrocarbon mass spectral fragmentations, but unambiguous experiments to determine the type and mechanism of these reactions are rare.[24,41] Several recent studies on hydrogen migration in oxygenated systems suggest that 1,2-, 1,4-, and 1,5-hydrogen migrations are facile while 1,3-hydrogen shifts are not.[36,42] In a few systems apparent 1,6, 1,7, 1,8, and higher order hydrogen migrations take place.[43] We have found evidence for 1,2 and 1,4 migrations in the ion–molecule reactions of deuterated propenes and cyclopropanes. We can exclude 1,3-hydrogen migration as a major contributor to isotopic scrambling in these systems. The scrambling data suggest that the $C_6H_{12}\cdot^+$ intermediate in the condensation rections of propene be capable of skeletal rearrangements *via* ions **6** and **7** and **8**. Fragmentation with loss of ethylene comes from a "four-center" cleavage of **6** and not from terminal cleavage in a linear structure such as **5**. Loss of methyl radical and ethylene both occur at rates competitive with isotopic scrambling. Examination of the fragmentation of a labeled 1,2-dimethylcyclobutane confirms that an ion of that structure can account for the products of the propene ion–molecule reaction. These observations support the "four-center" condensation mechanism postulated earlier to account for allene and propyne condensations.[3]

Isotopic scrambling in propene–cyclopropane condensation reactions can be explained by 1,2-, 1,4-, and 1,5-hydrogen migrations. Opening of the cyclopropane ring appears to occur on condensation with propene and leads to facile fragmentation to ethylene. The $C_3H_6\cdot^+$ ion from cyclopropane can be distinguished from that formed from propene by the product distributions in their ion–molecule reactions. Ion–molecule reactions have permitted the detection of a small amount of isotopic scrambling in the $CD_3CHCH_2\cdot^+$ ion at energies below the appearance potential for fragment ions. This is a new observation in rearrangement reactions and confirms predictions made on the basis of quasiequilibrium theory.

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(39) For an example of a reaction where energy redistribution may not be complete, see F. W. McLafferty, D. J. McAdoo, J. S. Smith, and R. Kornfeld, *ibid.*, **93**, 3720 (1971).

(40) F. W. McLafferty, T. Wachs, C. Lifshirtz, G. Innorta, and P. Irving, *ibid.*, **92**, 6867 (1970); J. C. Ton, *J. Phys. Chem.*, **75**, 1903 (1971), and references therein.

(41) F. W. McLafferty, *Top. Org. Mass Spectrom.*, **8**, 223 (1970).

(42) J. S. Smith and F. W. McLafferty, *Org. Mass Spectrom.*, **5**, 483 (1971); P. Brown, A. H. Albert, and G. R. Pettit, *J. Amer. Chem. Soc.*, **92**, 3212 (1970), and references therein.

(43) G. Eadon and C. Djerassi, *J. Amer. Chem. Soc.*, **91**, 2724 (1969), and references therein.